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ENHANCED OXIDATION OF PLATINUM IN ACTIVATED OXYGEN;  
IDENTIFICATION OF ACTIVE SPECIES

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# ENHANCED OXIDATION OF PLATINUM IN ACTIVATED OXYGEN

## II. IDENTIFICATION OF ACTIVE SPECIES

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Some time ago it was reported<sup>1</sup> that the oxidation rate of platinum in the temperature range above 800° C was enhanced in activated oxygen. It was also reported that the rate of the enhanced oxidation was directly proportional to the number of O atoms recombining on the platinum, and that the collision efficiency of the O atoms,  $\epsilon_0$ , was of the order of  $10^{-5}$ . Subsequently, it was indicated<sup>2, 3</sup> that the activation energy for the enhanced oxidation was near zero. This fact introduced the possibility<sup>3</sup> that the enhancement could be caused by some energetic species whose concentration was proportional to that of the O atoms but smaller by as much as  $10^{-5}$ . Several reactive particles are possible: vibrationally excited NO<sub>2</sub> molecules, formed from the O atoms by  $O + NO + O_2 \rightarrow NO_2^* + O_2$ ; ozone molecules, formed from the O atoms by  $O + O_2 + O_2 \rightarrow O_3 + O_2$ ; vibrationally excited O<sub>2</sub> molecules formed by  $O + O_3 \rightarrow O_2^* + O_2$ ; excited metastable O<sub>2</sub> molecules in the  $^1\Delta_g$ ,<sup>4, 5</sup>  $^1\Sigma_g^+$ ,<sup>6</sup> and  $^3\Sigma_u^+$  states formed in the discharge;<sup>7</sup> and excited metastable O atoms, most probably in the  $^1D$  state, formed in the discharge. The purpose of this communication is to describe some experiments that demonstrated that the normal O atom is the species causing the enhancement of the oxidation.



The experiments were conducted in the apparatus and by the general method described in reference 1. However, a microwave power supply with a slotted wave guide was used to activate the oxygen, and the apparatus was altered so that the partial pressure of O atoms could be determined by the  $\text{NO}_2^8$  and  $\text{NO}^9$  titration techniques.

In the first experiments the nitrogen impurity in the oxygen was varied and the effect on  $\epsilon_0$  was determined. Oxygen was used with nitrogen contents of 1, 0.5, 0.1, and  $< 0.01\%$ . In each case, 3% water vapor was added to the  $\text{O}_2$  because water vapor was required in the case of the high-purity  $\text{O}_2$  to obtain enough O atoms; we have shown previously<sup>1</sup> that the enhancement did not result from water vapor in the  $\text{O}_2$ . In none of these experiments could an effect due to  $\text{N}_2$  content be detected, indicating that  $\text{NO}_2^\dagger$  was not the species causing the enhanced oxidation. Similar results were obtained when the  $\text{N}_2$  content was 1, 0.5, or 0.1% and the  $\text{O}_2$  contained only 0.2% water vapor.

Two sets of experiments were performed in which the oxygen contained different percentages of water vapor; namely, 0.2% (dried at  $-80^\circ \text{C}$ ) and effectively zero (dried at  $-195^\circ \text{C}$ ). In both sets 1 percent  $\text{N}_2$  was added to the  $\text{O}_2$ , because it was required in the case of the dry  $\text{O}_2$  to obtain sufficient atoms. The partial pressure of NO formed in the arc from the  $\text{N}_2$  was determined from the afterglow by means of a photo tube and additions of NO.<sup>10</sup> If one assumes that all the  $\text{H}_2\text{O}$  is dissociated, and that  $\text{O}_3$  is removed by reaction with O atoms, NO,  $\text{O}_2(^1\Delta_g^{11})$  and  $^1\Sigma_g^{+8}$ , and

H atoms, it can be shown that the concentration of  $O_3$  in the "wet" oxygen should be less than 0.01 of that in the dry oxygen. This is due to the extremely high rate of the reaction sequence<sup>6,9</sup>  $H + O_3 \rightarrow O_2 + OH$ ,  $O + OH \rightarrow H + O_2$ , which provides an H atom catalyzed removal of ozone. The difference in the average  $\epsilon_0$  of the two sets of data was within experimental error, which indicated that  $O_3$  was not causing the enhanced oxidation. These experiments also eliminate the  $O_2^{\dagger}$  molecule as a possibility, because it is formed from the  $O_3$ .

It was then demonstrated that the major portion of the enhancement resulted from the action of the O atom. Experiments were performed in the usual way except that just enough  $NO_2$  was added upstream of the platinum specimen to remove all the O atoms, the removal being indicated by the extinguished O-NO afterglow. Metastable  $O_2$  molecules should not be decreased by such a treatment.<sup>6,12</sup> The enhanced oxidation rate was only 5% of the rate when the O atoms were not removed. The 5% remaining may have resulted from metastable molecules or from incomplete removal of O atoms. In either case, metastable molecules can be eliminated as the important species causing the enhanced oxidation. It may be noted that the heat released to the platinum specimen when the O atoms were recombining on it was identical to that when the O atoms were removed by titration with  $NO_2$ . Apparently, vibrationally excited  $O_2$  molecules were formed in large numbers by the reaction  $O + NO_2 \rightarrow NO + O_2^{\dagger}$  and these were deactivated by the hot platinum

surface. This is a further indication that the  $O_2^{\ddagger}$  molecules do not cause the enhanced oxidation.

While we have shown that the enhanced oxidation results from the  $O$  atom, it is necessary to determine whether the normal  $^3P$  or the metastable  $^1D$  oxygen atom is responsible. There is no experimental evidence for the existence of the  $^1D$  oxygen atom in activated oxygen. It has not been detected by mass spectrographic <sup>4, 5</sup> nor by paramagnetic resonance methods.<sup>13</sup> In addition, the slow rate of reaction at 25° C between activated oxygen and hydrogen<sup>14, 15</sup> indicates the absence of the  $^1D$  oxygen atom.<sup>16</sup> Nevertheless, it might be possible that the metastable atom is present to the extent of 1 part in  $10^5$ .

It would be expected that in a discharge the greater the power, the greater the fraction of electronically excited species produced. Kaufman and Kelso<sup>17</sup> have demonstrated this for excited oxygen molecules, and Clyne, Thrush, and Wayne<sup>6</sup> have corroborated their results. In our oxidation experiments, we have never been able to detect any influence of the amount of power used for the discharge on  $\epsilon_0$ . Microwave discharges ranging from 30 to 1000 wats were used, and even 60 cycles A.C. discharges between aluminum electrodes with currents ranging from 30 to 100 ma were used. These results seem to rule out the  $^1D$  oxygen atom and indicate that the enhanced oxidation is caused by the normal oxygen atom. This conclusion is supported by some recent work of Rosner and Allendorf who have simulated our oxidation experiments but used tungsten<sup>18</sup>

and molybdenum<sup>19</sup> specimens. Their results are very similar to ours except that the collision efficiencies are of the order of 0.1 for the O atom with these metals. Obviously, the <sup>1</sup>D oxygen atom cannot be the cause of the enhanced oxidation in the case of these metals. The normal O atom must be involved.

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